



यज्ञाद्यान् लभते ज्ञानम्
ESTD 1881

Reaction Mechanism



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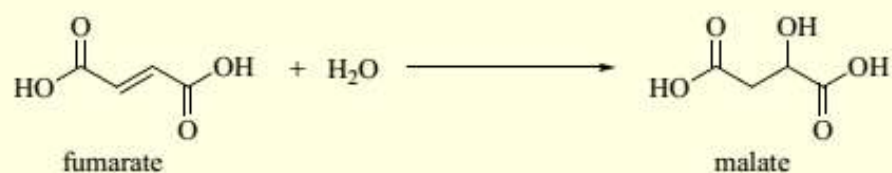


Dr. Biswajit Panda

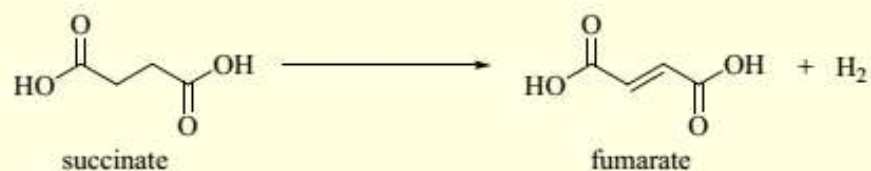
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Date: 28.09.2020

Types of Organic Reactions

1. Addition Reactions: $A + B \rightarrow C$



2. Elimination Reactions: $D \rightarrow E + F$



3. Substitution Reactions: $G-H + I^{\ominus} \rightarrow G-I + H^{\ominus}$



Types of Organic Reactions

4. Rearrangements: J \rightarrow K



How do these reactions occur?

Why do these reactions occur?

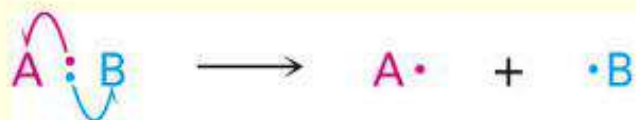
We must explain how electrons are exchanged during the formation of new bonds and breaking of old bonds.

How Reactions Occur

Symmetrical Bond Making/Breaking (homolytic process)

vs

Unsymmetrical Bond Making/Breaking (heterolytic process) - POLAR Reactions



Symmetrical bond-breaking (radical):
one bonding electron stays with each product.



Unsymmetrical bond-breaking (polar):
two bonding electrons stay with one product.

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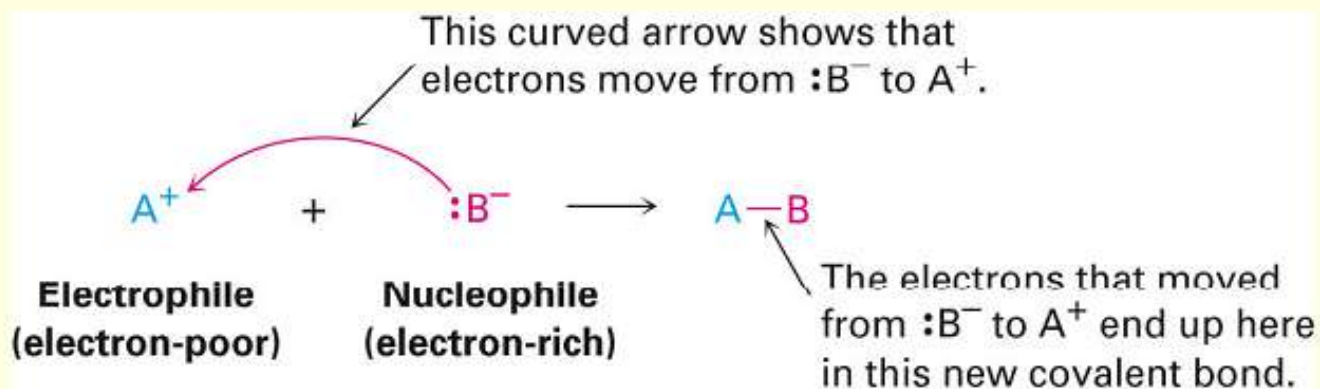
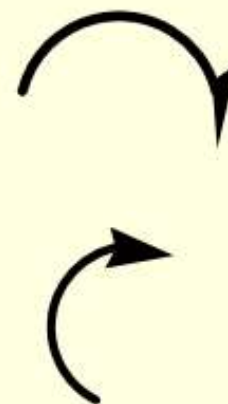
Symmetrical bond-making (radical):
one bonding electron is donated by each reactant.



Unsymmetrical bond-making (polar):
two bonding electrons are donated by one reactant.

Indicating Electron Movement in Reaction Mechanisms

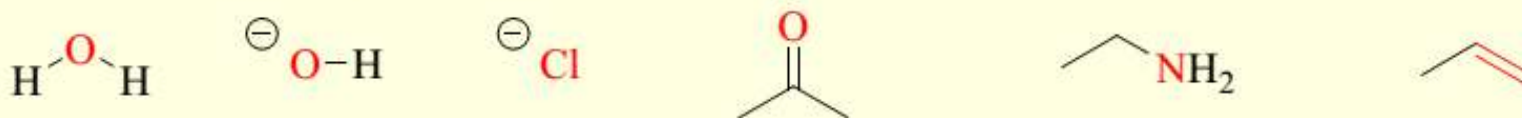
- Curved arrows indicate breaking and forming of bonds
- Arrowheads with a “half” head (“fish-hook”) indicate homolytic and homogenic steps (called ‘radical processes’)
- Arrowheads with a complete head indicate heterolytic and heterogenic steps (called ‘polar processes’)



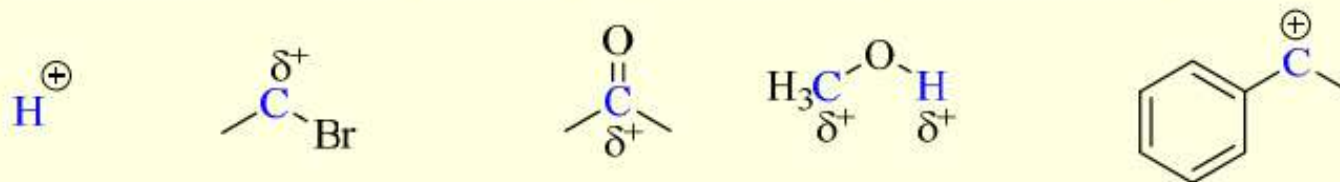
Polar Reactions

Opposite charges attract

- Nucleophiles (electron rich sites, seek nucleus) - have lone pair of electrons or C=C bond



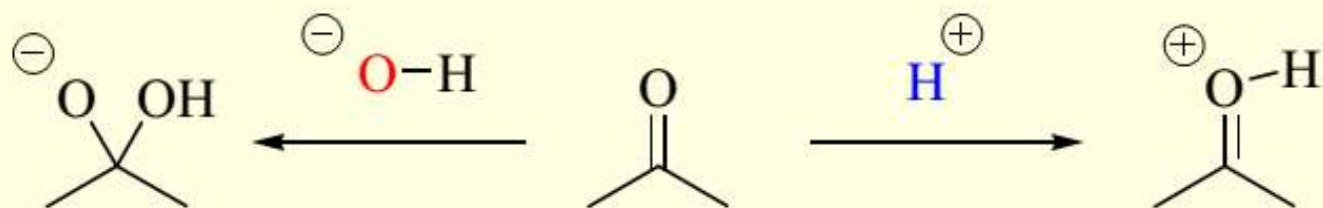
- Electrophiles (electron poor sites, seek electrons) - have formal positive charge or partial positive charge via bond dipole



Nucleophiles are synonymous with Lewis Bases, Electrophiles are synonymous with Lewis Acids, Polar reactions are Lewis Acid-Base reactions.

Nucleophiles and Electrophiles

Note that compounds can be nucleophilic and electrophilic. You must look at specific atoms and what the compound is reacting with to determine how it will react:



Judging relative 'strengths' of Nuc and E⁺

Strong Nuc

less stable anion

more stable anion

lone pair less EN atom

lone pair more EN atom

C=C

Weak Nuc

Strong E⁺

less stable cation

more stable cation

neutral atom incomplete octet

large partial positive atom

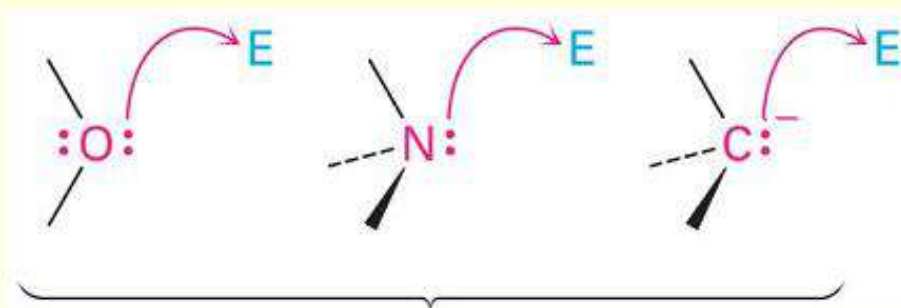
small partial positive atom

Weak E⁺

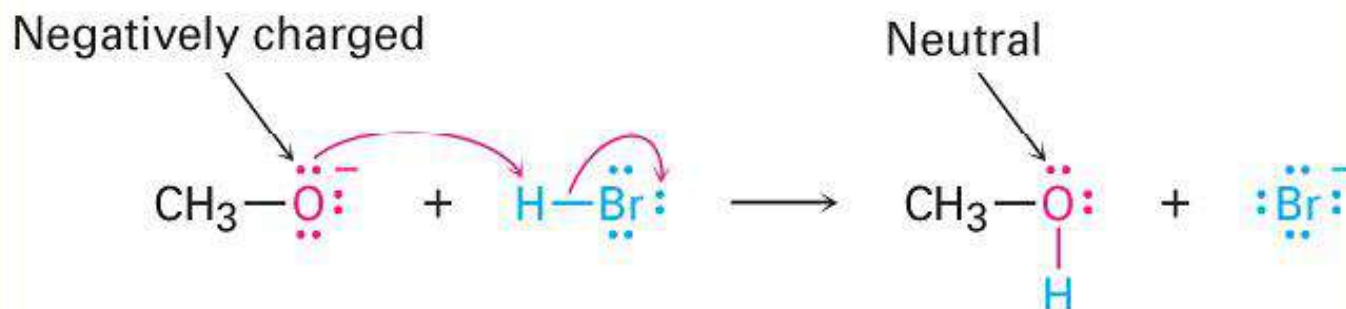
Drawing Reaction Mechanisms

Use of curved arrows to show electron movement in bond making and bond breaking process. For polar reactions, electrons move as a pair. Note that charges must also balance.

- The arrow goes from the nucleophilic reaction site to the electrophilic reaction site

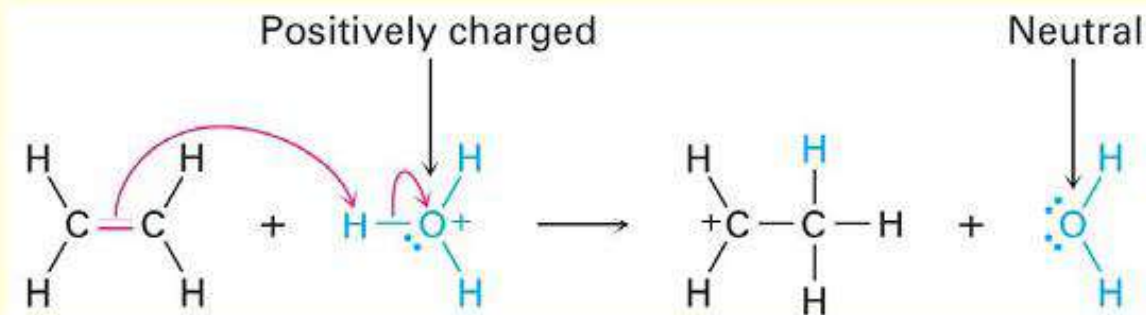


- The nucleophilic site can be neutral or negatively charged

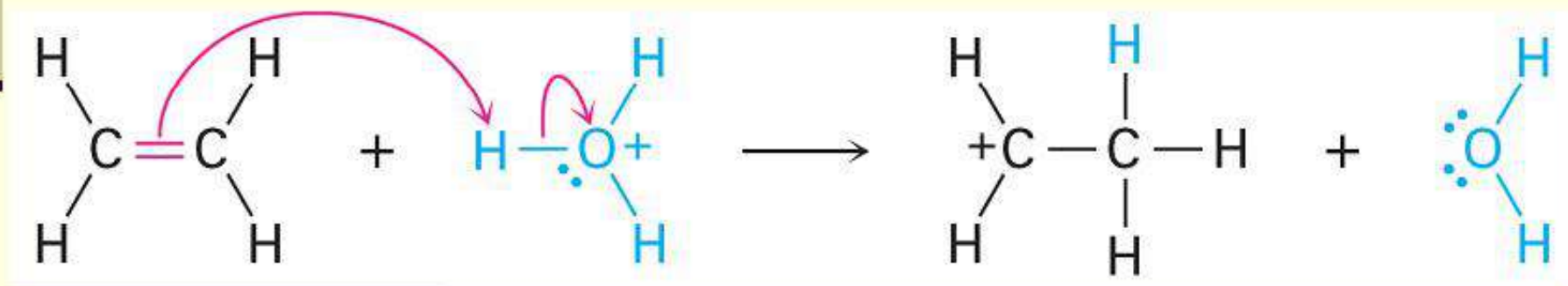


Drawing Reaction Mechanisms

- The electrophilic site can be neutral or positively charged

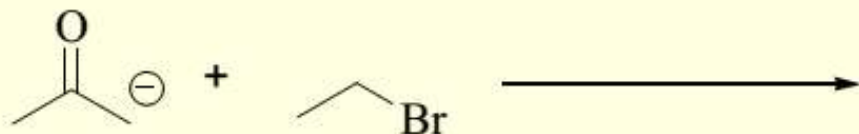
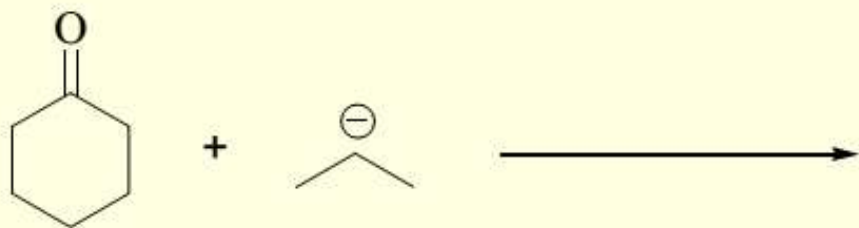
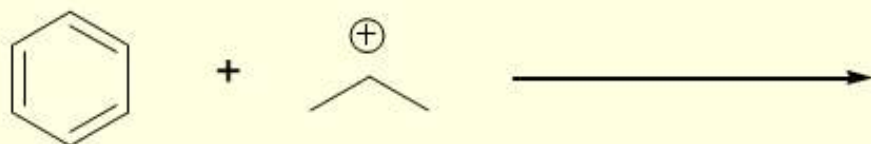


- The octet rule must be followed

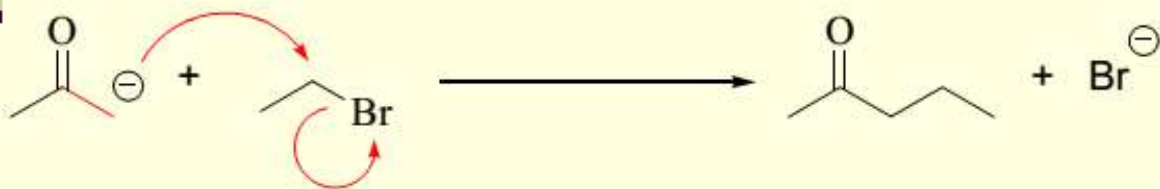
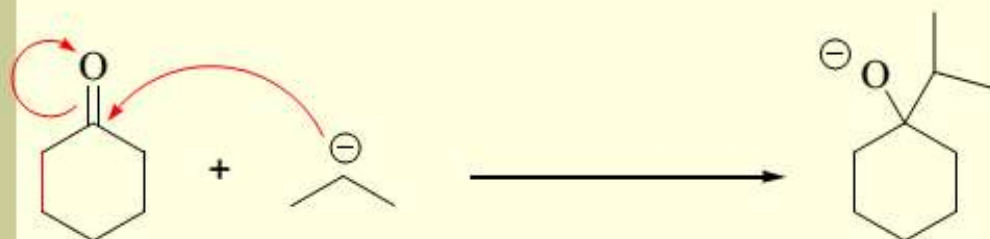
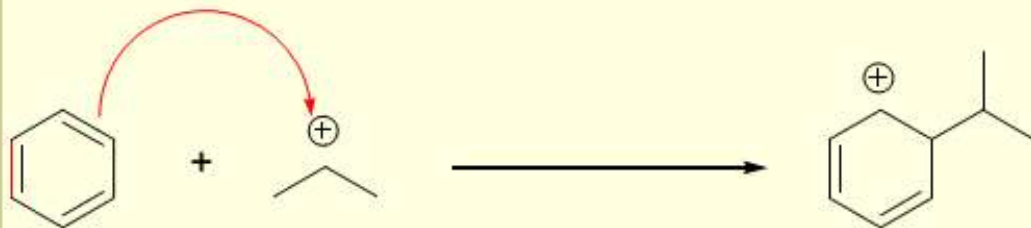


- (never have +2 or -2 charge on a single atom)

Drawing Reaction Mechanisms

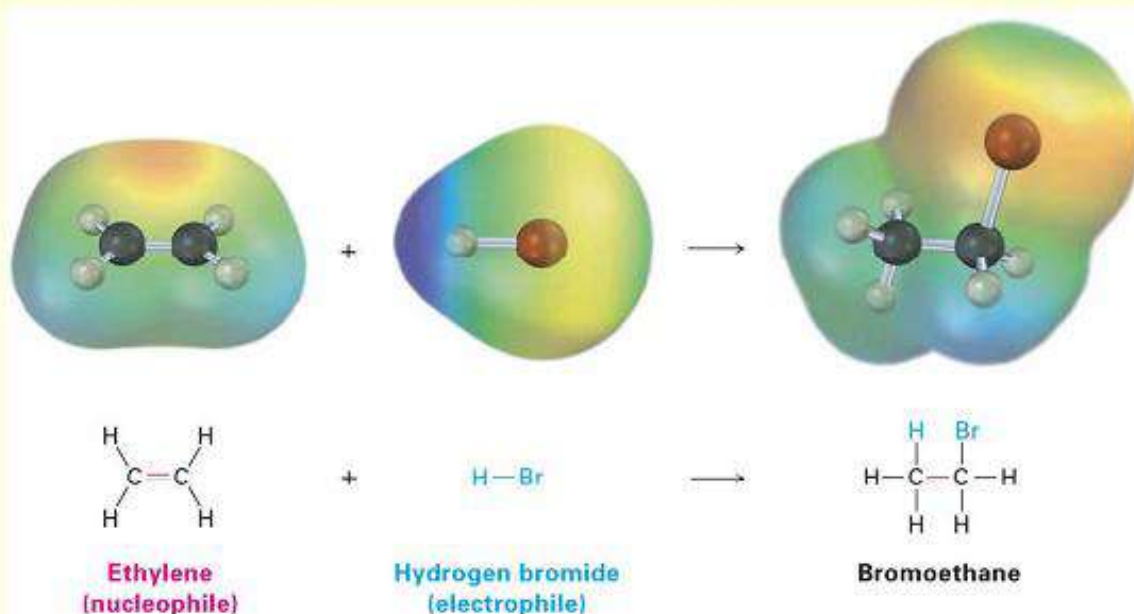


Drawing Reaction Mechanisms



An Example of a Polar Reaction: Addition of HBr to Ethylene

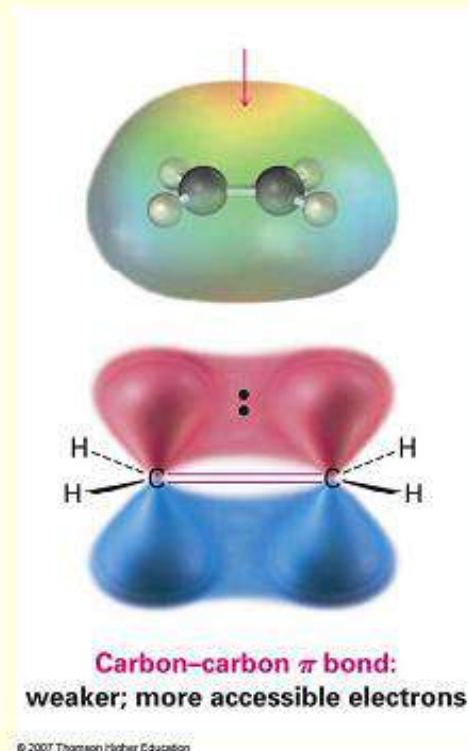
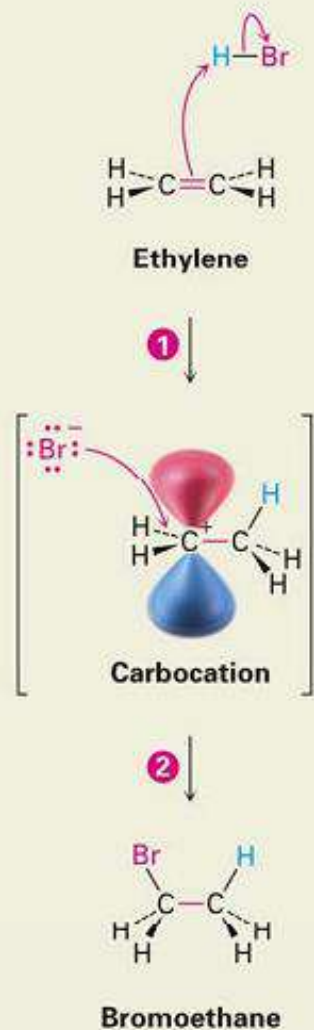
- HBr adds to the π part of C-C double bond
- The π bond is electron-rich, allowing it to function as a nucleophile
- H-Br is electron deficient at the H since Br is much more electronegative, making HBr an electrophile



Mechanism of Addition of HBr to Ethylene

1 A hydrogen atom on the electrophile HBr is attacked by π electrons from the nucleophilic double bond, forming a new C-H bond. This leaves the other carbon atom with a + charge and a vacant p orbital. Simultaneously, two electrons from the H-Br bond move onto bromine, giving bromide anion.

2 Bromide ion donates an electron pair to the positively charged carbon atom, forming a C-Br bond and yielding the neutral addition product.



Why Reactions Occur

All organic reactions we will study will reach equilibrium that favors the more stable side. In most cases, these will be reaction products as written from left to right (note, however, sometimes you must predict which side is favored as in acid-base reactions).

$$\Delta G^{\circ} = -RT \ln K_{\text{eq}} = \Delta H - T\Delta S$$

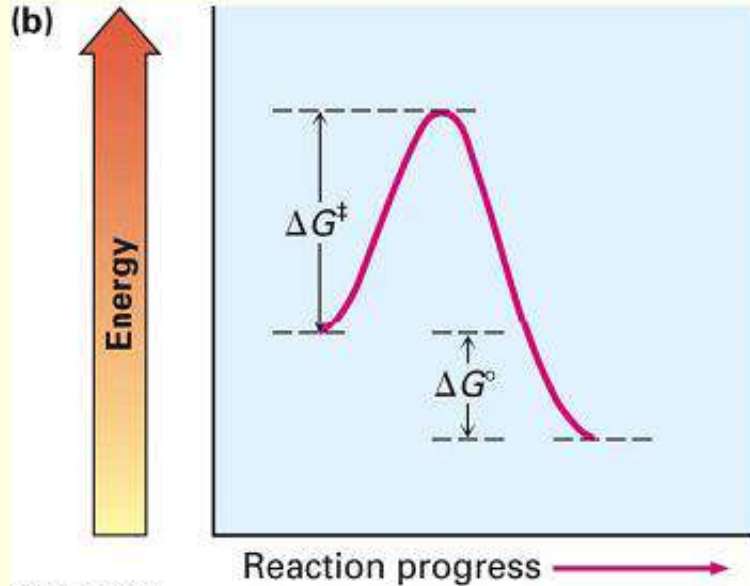
If $K_{\text{eq}} > 1$, energy is released to the surroundings
(**exergonic** reaction, negative value of ΔG° , reaction favored)

If $K_{\text{eq}} < 1$, energy is absorbed from the surroundings
(**endergonic** reaction, positive value of ΔG° , reaction not favored)

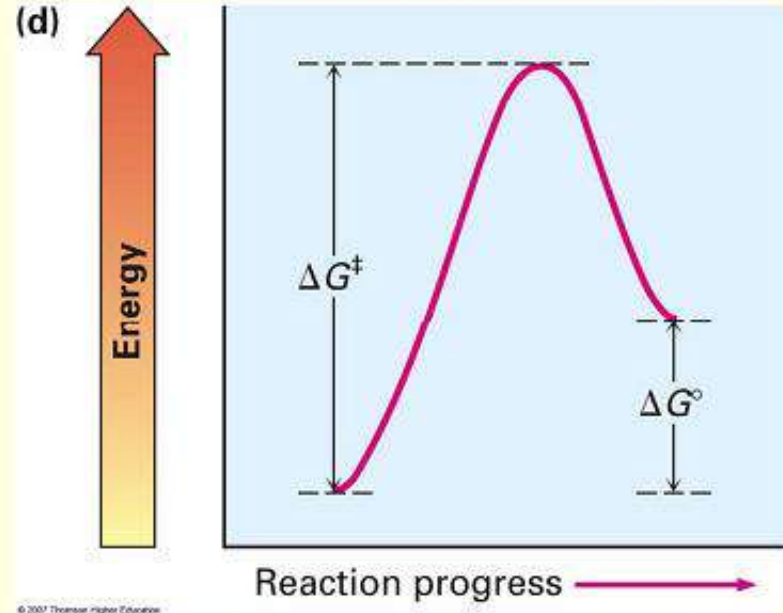
Energy changes in a reaction are illustrated by Energy Diagrams

Reaction Energy Diagrams

One Step Reactions:



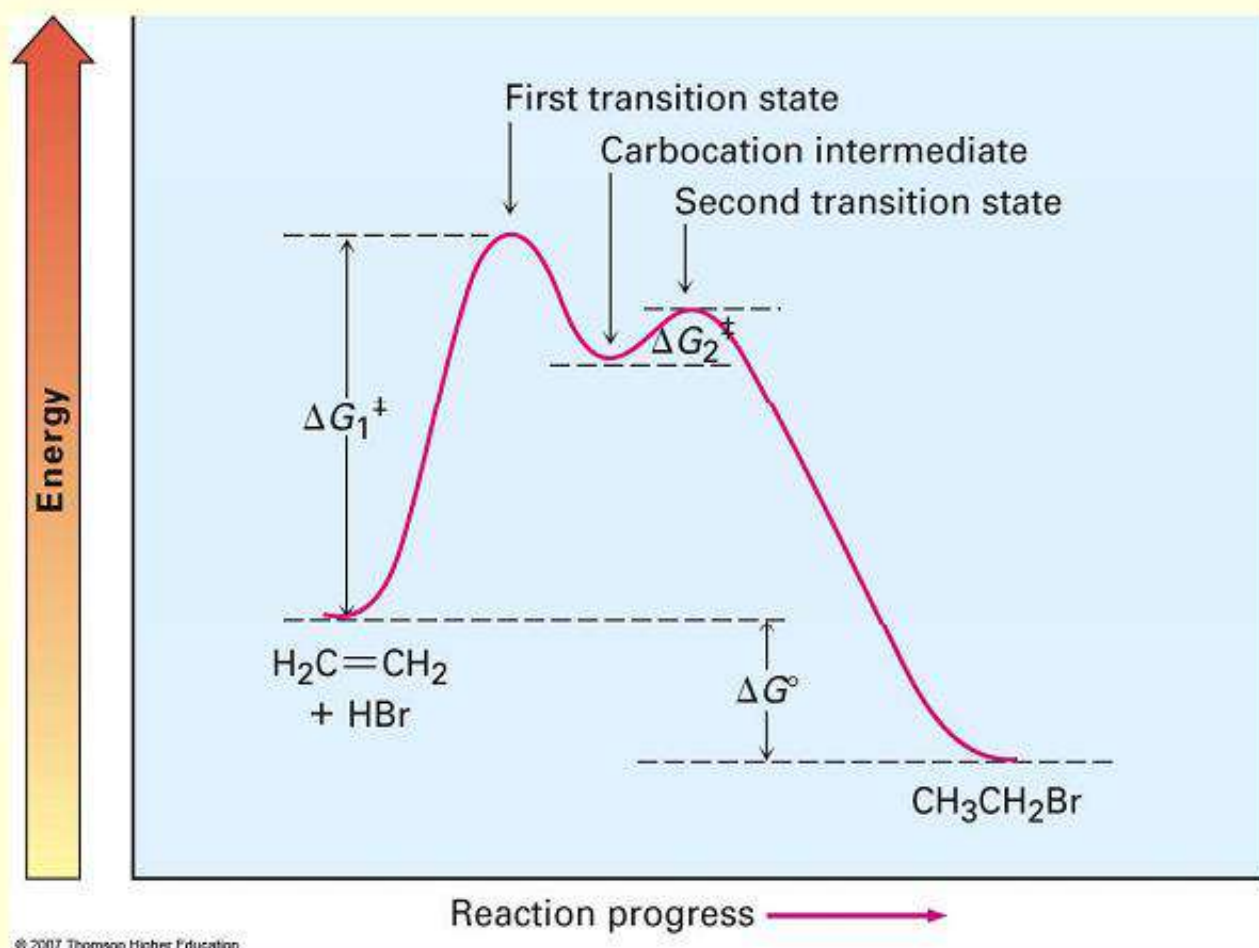
Exergonic ($-\Delta G$)
(thermo favored)



Endergonic ($+\Delta G$)
(thermo not favored)

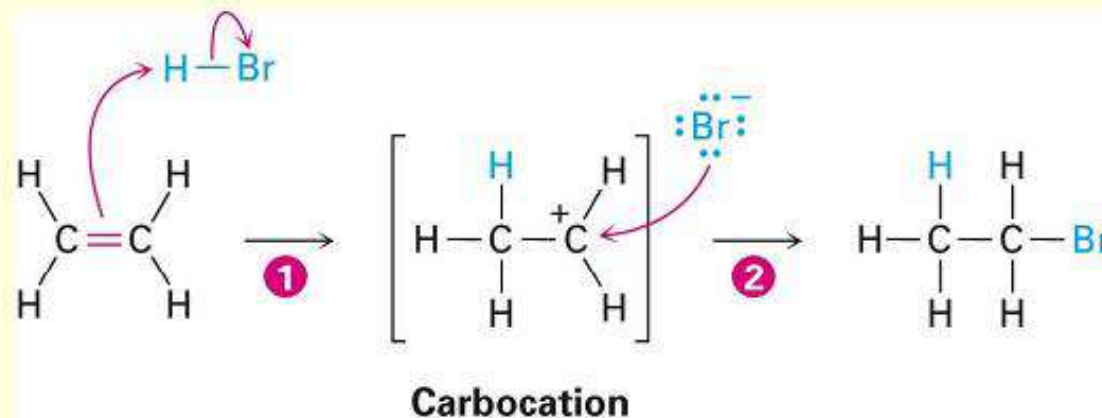
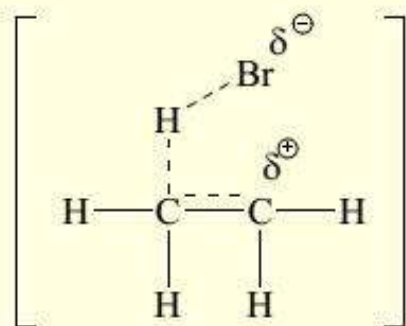
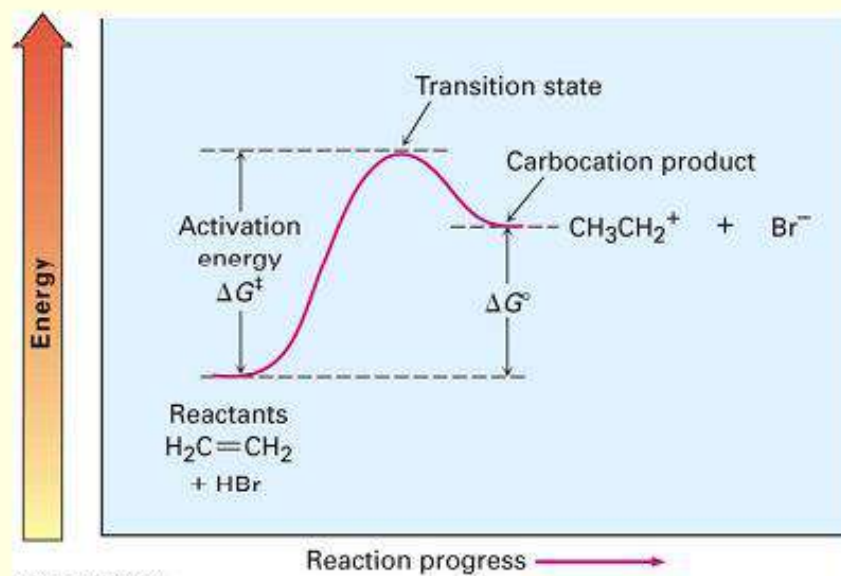
Reaction Energy Diagrams

Multiple Step Reactions:



Reaction Energy Diagrams

- The highest energy point in a reaction step is called the **transition state**
- The energy needed to go from reactant to transition state is the **activation energy** (ΔG^\ddagger)



Reaction Energy Diagrams

- If a reaction occurs in more than one step, it must involve species that are neither the reactant nor the final product
- These are called **reaction intermediates** or simply “intermediates”
- Each step has its own free energy of activation
- The complete diagram for the reaction shows the free energy changes associated with an intermediate

